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(17) UV-vis ($CHCl_3$, λ in nm): 439, 533, 569, 611, and 669 (ref 14b: 438, 530, 565, 606, 655 in C_6H_6.). ^1H NMR ($CDCl_3$, δ in ppm): 8.50 (s, pyrrole-H), −3.32 (s, N-H).
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(23) The polymer obtained with **1a** was rich in isotactic sequences (i:s = 0.68:0.32, I:H:S = 0.46:0.41:0.13, as determined by ^{13}C NMR (see Oguni, N.; Lee, K.; Tani, H. *Macromolecules* **1972**, *5*, 819), while that with **2a** was virtually atactic (i:s = 0.49:0.51, I:H:S = 0.23:0.50:0.27).
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Registry No. **1a**, 71102-37-9; **1c**, 66945-43-5; **2a**, 126296-46-6; **2c**, 126296-56-8; **3a**, 126296-47-7; **3c**, 126296-57-9; **4a**, 126296-48-8; **4c**, 126296-58-0; **5a**, 126296-49-9; **6a**, 126296-50-2; **7a**, 126296-51-3; **8a**, 126296-52-4; **8c**, 126296-59-1; **9a**, 126296-53-5; **9c**, 126296-60-4; **10a**, 126296-54-6; **10c**, 126296-61-5; **11a**, 126296-55-7; PO (SRU), 25322-69-4; β-PL (homopolymer), 25037-58-5; β-PL (SRU), 24938-43-0; δ-valerolactone (homopolymer), 26354-94-9; δ-valerolactone (SRU), 26499-05-8.

Synthesis and Characterization of Poly(1,4-phenylenevinylene) Derivatives

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ABSTRACT: We report the synthesis of functionalized poly(*p*-phenylenevinylenes), in which α and β positions are substituted with oxygen-containing groups. These functionalized poly(*p*-phenylenevinylenes) were synthesized by the reaction of polybenzoin, synthesized by the benzoin-type reaction of terephthalaldehyde, with Schlosser's base, KO*t*-Bu/*n*-BuLi, to generate a polydianion, which on further reaction with acetyl chloride and dimethyl sulfate yields the corresponding poly(1,4-phenylenevinylene α,β-diol diacetate) and poly(1,4-phenylene-α,β-dimethoxyvinylene), respectively. These materials were characterized by IR, NMR, and elemental analysis. The conductivity was measured in the pristine state ($\sim 10^{-10}$ S/cm) as well as after doping with iodine ($\sim 10^{-6}$ S/cm).

Poly(1,4-phenylenevinylene) (PPV) forms the basis of an important class of nondegenerate, conducting polymers in which conjugation is extended by the aromatic rings included directly in the chain.[1] In this class of polymers two structures arising due to resonance—benzenoid and quinonoid—do not have the same energy. The quinonoid structure has higher energy than the benzenoid structure. Other examples of such nondegenerate systems are polyphenylene, polypyrrole, and polythiophene.[1]

PPV was first synthesized by Drefahl et al.[2] and later by Kossmehl et al.[3] using the Wittig reaction. Kanbe et al.[4] and Wessling et al.[5] used sulfonium salts to synthesize the PPV, and Lillya et al.[6] have used both the Wittig reaction and the dehydrohalogenation reaction to synthesize PPV. Moshchinskaya et al.[7] have synthesized PPV through the ammonium salts, whereas Karasz et al.[8-11] have studied the sulfonium reaction extensively to make PPV and its analogues with substituents on the aromatic ring.

PPVs synthesized by the Wittig reaction and by dehydrohalogenation are insoluble and infusible and probably of low molecular weight (DP 11).[11] However, the use

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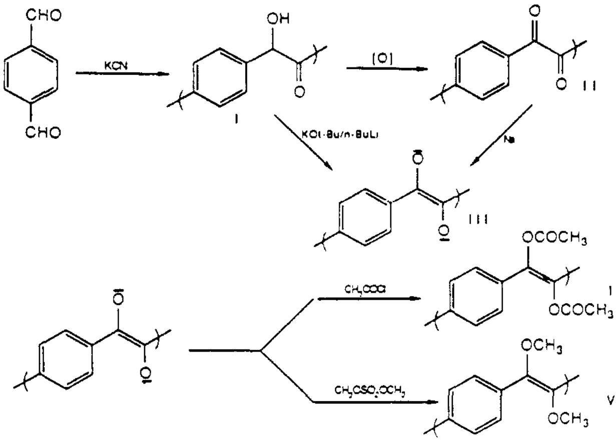
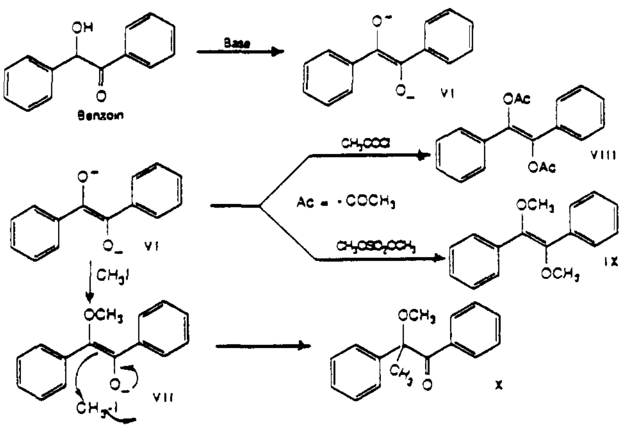
Scheme I
Reactions of the Polydianion of Polybenzoin (New Route To Synthesize PPV Analogues)



Scheme II
Reactions of Benzoin Dianion



of sulfonium salts in the preparation of PPV results in high molecular weight polymers (DP 2000).[9b]

The electrical properties of PPV were first investigated by Lapitskii.[12] In the pristine state, PPV is an insulator (conductivity ca. 10^{-12} S/cm). However, on doping with AsF_5, the conductivity increases to 14 S/cm, depending upon the orientation of the polymer and method of preparation. Highly oriented films seem to give higher conductivity than unoriented films possibly because of chain extension.[6] Also, photoconductivity has been observed in highly oriented PPV films.[13] PPV does not show any increase in conductivity on exposure to iodine,[8] but poly(2,5-dimethoxy-1,4-phenylenevinylene) shows an increase in 13 orders of magnitude, in electrical conductivity, on doping with iodine.[10]

In this paper we describe the synthesis of some new derivatives of PPV by a new approach that involves the reaction of poly(1,4-phenylene-1-oxo-2-hydroxyethylene) (I) with a strong base to produce the polydianion, which then reacts as a nucleophile with dimethyl sulfate and with acetyl chloride (Scheme I).

Experimental Section

All glassware was dried at 150 °C and assembled under Ar; solvents THF (Fisher) and HMPT (Aldrich) were first refluxed over CaH_2 or Na for 12–24 h and freshly distilled under N_2 or vacuum before use; all transfer operations of KO*t*-Bu (Aldrich), benzoin (Aldrich), solvents, solutions, and *n*-butyllithium (Aldrich) were performed under dry N_2 or Ar. I was stirred in HMPT for 2–3 h to obtain a homogeneous solution before its addition to the base solution.

Poly(1,4-phenylene-1-oxo-2-hydroxyethylene) (I).[14] In a 500-mL round-bottom flask were placed 100 mL of methanol, terephthalaldehyde (8.6 g, 0.064 mol), and 100 mL of water. To this solution, under stirring, was added dropwise a solution of NaCN (4 g, 0.082 mol), 25 mL of methanol, and 25 mL of water. The contents turned cherry red soon after the addition of the NaCN solution. A precipitate formed after 30 min of stirring, and the resulting reaction mixture was stirred overnight. The precipitate was filtered, washed with 1000 mL of water and 100 mL of methanol, and dried under vacuum at 100 °C overnight: yield 4.92 g (57%, pale yellow; T_m, 230–280 °C; DP, ~6 (end-group analysis by NMR[5]); IR (KBr pellet) 3500 (OH stretch), 1680 (C=O stretch), 1600 (conjugated C=C stretch), 1250 (C-O stretch, C-OH), 825 (CH bend, benzene ring) cm^{-1}; ^1H NMR (DMSO) δ 7.2–8.2 (4 H, benzene ring), 6 (2 H, -CH and -OH).

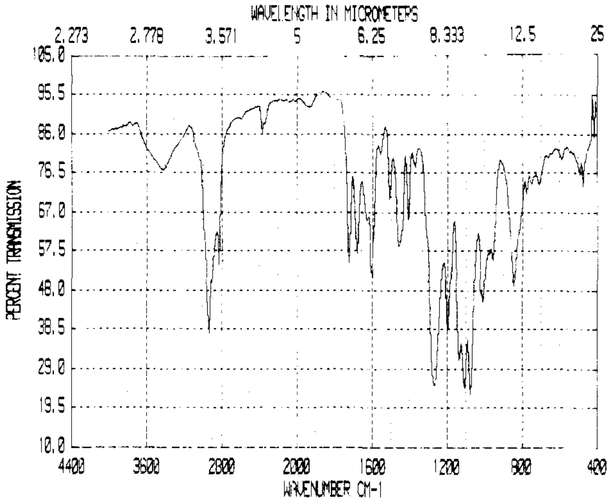


Figure 1. IR spectrum of poly(*p*-phenylene-α,β-dimethoxyvinylene).

Poly(1,4-phenyleneoxalyl) (II).[14] I (1.7 g, 0.013 mol) was refluxed in 50 mL of dilute HNO_3 (83%, v/v) for 3 days until the hydroxyl band disappeared from the IR spectrum. The product was filtered, washed with water until acid free and then with methanol, and dried under vacuum at 60 °C overnight to yield a lemon yellow material: yield 1.5 g (87%); T_m, not observed to 300 °C; IR (KBr pellet) 1700 (C=O stretch), 1590 (C=C stretch, benzene ring), 825 (C–H bend, benzene ring) cm^{-1}; insoluble in all solvents.

Schlosser's Base.[15] Into a three-necked flask, fitted with a N_2 or an Ar inlet, a magnetic stirrer, an addition funnel containing BuLi/hexane, and a small glovebag containing a KO*t*-Bu vial, was distilled 100 mL of THF. After the transfer of KO*t*-Bu (0.77 g, 6.9 mmol), the flask was cooled to −78 °C and the *n*-butyllithium (4.4 mL, 1.6 M, 7.0 mmol) was added dropwise. The color of the solution first turned pale yellow and then became lemon yellow after 15 min of stirring.

Benzoin Dianion (VI). After the above solution of Schlosser's base was stirred for 20 min at −78 °C, benzoin (0.58 g, 2.7 mmol) was transferred into the flask, whereby the contents turned orange. When this suspension was allowed to come to room temperature, its color was red. This suspension, VI, was used as such in subsequent reactions.

α,β-Stilbenediol Diacetate (VIII). The above dianion suspension VI was cooled to −78 °C, and freshly distilled acetyl chloride (1.3 mL, 1.5 mmol) was added dropwise. The reaction mixture was then stirred for 15 h at room temperature. After concentrating the reaction mixture on a rotary evaporator, water was added to yield a white precipitate. The precipitate was filtered, washed with water, and recrystallized from a methanol–water mixture: yield 0.57 g (70%); T_m 118–119 °C (lit.[16] T_m 118–119 °C (cis isomer), 154–156 °C (trans isomer)); IR (KBr pellet) 3100 (=CH stretch), 2950 (saturated CH stretch), 1760 (ester C=O stretch), 1600 (conjugated C=C stretch), 1250 (COC stretch), 750 and 690 (monosubstituted benzene ring, CH bending) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 10 H, aromatic), 2.0 (s, 6 H, CH_3).

α,β-Dimethoxystilbene (IX). The dianion solution, VI, made from 5.0 mL (2 M, 10 mmol) of *n*-butyllithium, 1.1 g (10 mmol) of KO*t*-Bu, and 0.42 g (2.0 mmol) of benzoin, was cooled to −78

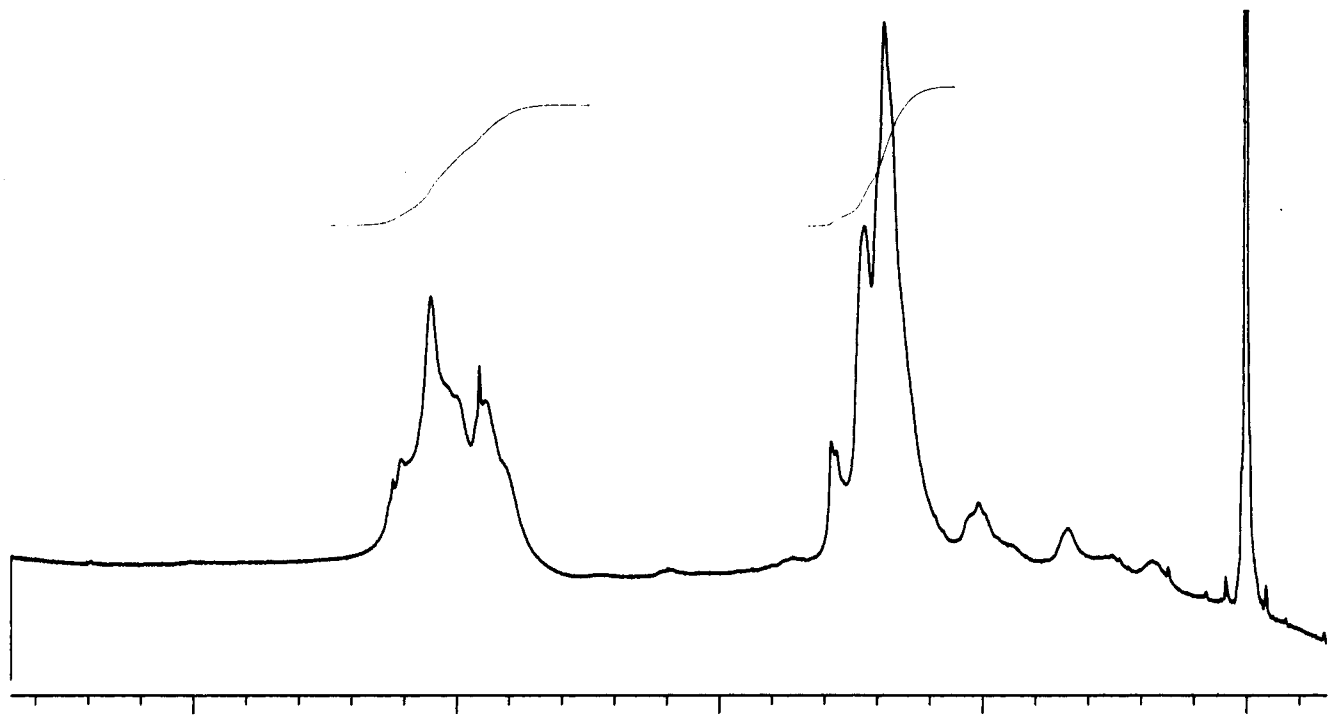


Figure 2. ^{1}H NMR spectrum of poly(*p*-phenylene-α,β-dimethoxyvinylene).

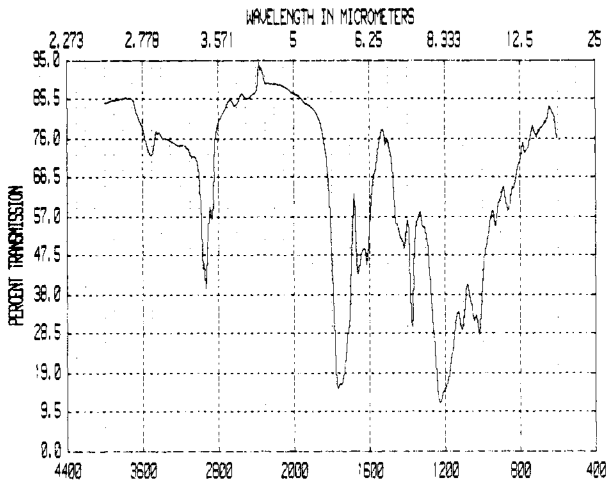
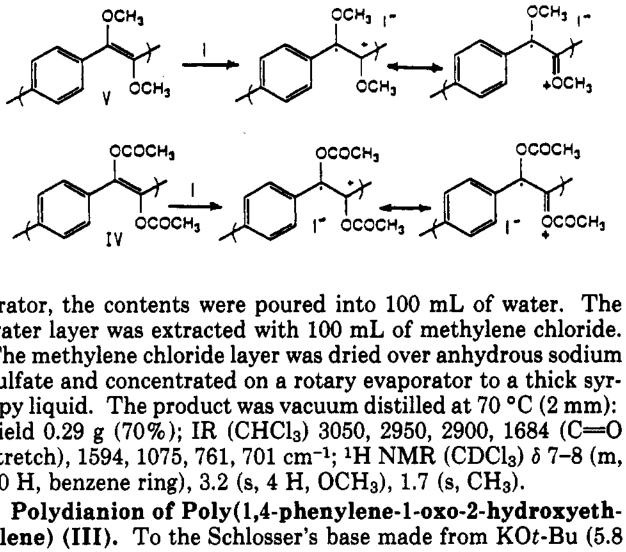


Figure 3. IR spectrum of poly(*p*-phenylenevinylene-α,β-diol diacetate).

Scheme III



°C, and freshly distilled dimethyl sulfate (3.0 mL, 13 mmol) was added dropwise. The reaction mixture was stirred for 15 h at room temperature. After concentrating on a rotary evaporator, water was added to the reaction mixture. The product was extracted with chloroform, and the chloroform layer was dried over anhydrous sodium sulfate and concentrated on a rotary evaporator, whereby a viscous mass was recovered. To this viscous mass was added hexane, and the product precipitated as a white crystalline material. It was filtered, washed with hexane, and dried overnight under vacuum at room temperature: yield 0.19 g (50%); T_m 95–98 °C (lit.[17,18] T_m 66–67 °C (configuration unspecified), 123 °C (cis), and 88 °C (trans)); IR (KBr pellet) 3100 (=CH stretch), 2950 (saturated CH stretch), 1600 (conjugated C=C stretch), 750 and 690 (CH bending, benzene ring) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.1 (s, 10 H, benzene ring), 3.5 (s, 6 H, OCH$_3$) (lit.[18] ^{1}H NMR δ 7.02 and 3.51 (cis), 7.45 and 3.23 (trans).

Reaction of Benzoin Dianion with Methyl Iodide (X). The dianion solution, VI, made from 5.0 mL (2 M, 10 mmol) of *n*-butyllithium, 1.9 g (170 mmol) of KO*t*-Bu, and 0.39 g (16 mmol) of benzoin, was cooled to −78 °C. To this solution, was added dropwise 7.0 mL (0.11 mol) of CH$_3$I. The contents were stirred for 12 h. After the solution was concentrated on a rotary evaporator, the contents were poured into 100 mL of water. The water layer was extracted with 100 mL of methylene chloride. The methylene chloride layer was dried over anhydrous sodium sulfate and concentrated on a rotary evaporator to a thick syrupy liquid. The product was vacuum distilled at 70 °C (2 mm): yield 0.29 g (70%); IR (CHCl$_3$) 3050, 2950, 2900, 1684 (C=O stretch), 1594, 1075, 761, 701 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7–8 (m, 10 H, benzene ring), 3.2 (s, 4 H, OCH$_3$), 1.7 (s, CH$_3$).

Polydianion of Poly(1,4-phenylene-1-oxo-2-hydroxyethylene) (III). To the Schlosser's base made from KO*t*-Bu (5.8 g, 52 mmol) and *n*-BuLi (26 mL, 2 M, 52 mmol), after stirring at −78 °C for 20 min, was added a I-HMPT (1.3 g, 10 mmol) solution. The contents turned black and this black suspension was allowed to come to room temperature before the addition of acetyl chloride, methyl iodide, or dimethyl sulfate.

Poly(1,4-phenylene-1,2-dimethoxyethylene) (V). To the above polydianion III solution was added dropwise at room temperature freshly distilled dimethyl sulfate (13 mL, 140 mmol), and the mixture was stirred for 15 h at room temperature. It was concentrated on a rotary evaporator to a syrup, which was poured into 200 mL of water under stirring to give a yellow precipitate. This yellow material was dissolved in chloroform, dried over anhydrous sodium sulfate, and column chromatographed (SiO$_2$–CHCl$_3$). The first fraction (~100 mL) was collected, and this chloroform solution was concentrated and poured into 100 mL of ether to yield a yellow precipitate. The precipitate was filtered, washed with ether, and dried overnight at 45 °C under vacuum: yield 0.19 g (12%); T_m 160–170 °C; IR (CHCl$_3$) 3100 (=CH stretch), 2950 (saturated CH stretch), 1722, 1600 (conjugated C=C stretch), 1250 (COC stretch, ether), 846 (benzene ring, CH bending) cm^{-1} (Figure 1); ^{1}H NMR (CDCl$_3$) δ 7–8 (br, 4.7 H, benzene ring), 3.9 (br, 6 H, OCH$_3$) (Figure 2). Elementary analysis of this material was unsatisfactory; a sam-

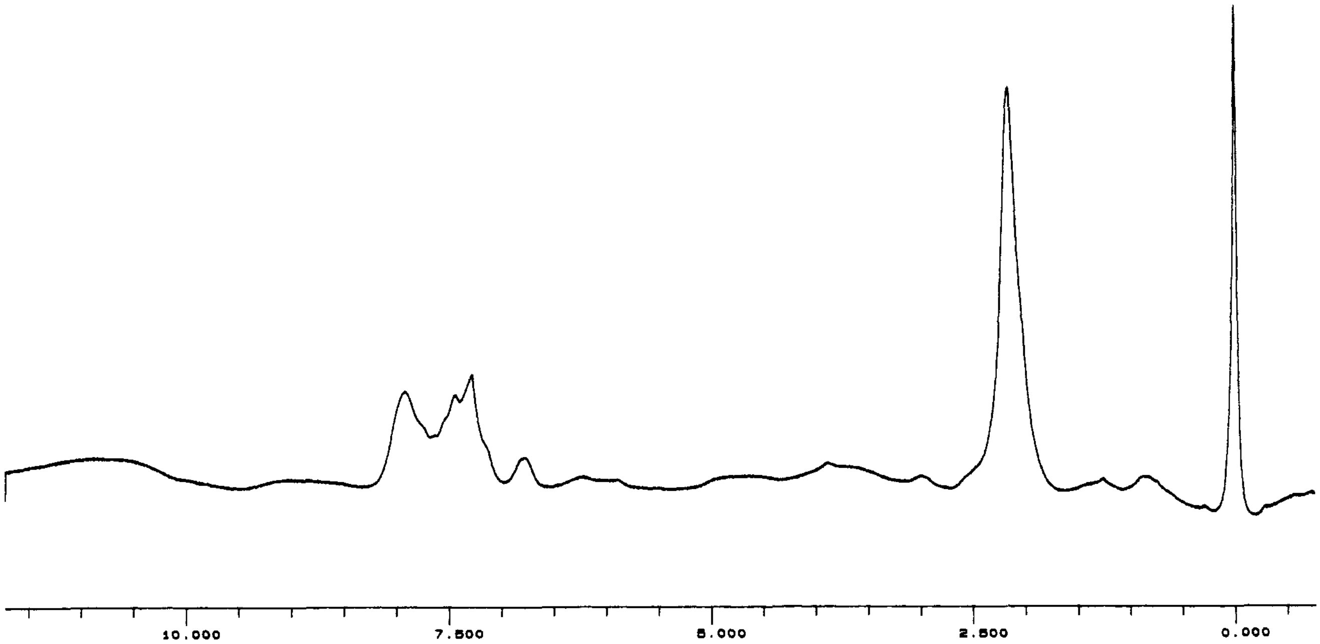


Figure 4. ^1H NMR spectrum of poly(*p*-phenylenevinylene-α,β-diol diacetate).

ple burned slowly (ca. 3 min on the hottest part of the Bunsen burner flame) to leave no ash.

Poly(1,4-phenylene-1,2-diacetoxyethylene) (IV). The dianion solution, made from 26 mL (2 M, 52 mmol) of *n*-butyllithium, 5.1 g (46 mmol) of KO*t*-Bu, and 1.3 g (10 mmol) of I, was cooled to −78 °C, and freshly distilled acetyl chloride (15 mL, 98 mmol) was added dropwise. The reaction mixture was treated as above for V to produce a yellow precipitate, which, after drying, chromatographing, and concentrating, was filtered, washed with ether, and dried overnight at 45 °C under vacuum: yield 0.25 g (12%); T_m 174–85 °C, 300 °C dec; IR ($CHCl_3$) 3100 (=CH stretch), 2950 (saturated CH stretch), 1760 (C=O stretch, ester), 1600, 1250 (COC stretch, ester), 846 cm^{-1} (Figure 3); ^1H NMR ($CDCl_3$) δ 7–8 (br, 4.6 H, benzene ring), 2.2 (br, 6 H, CH_3) (Figure 4). Elementary analysis of this material was unsatisfactory; a sample burned slowly (ca. 3 min to burn completely).

Reaction of the Polydianion (III) with Methyl Iodide. The dianion solution, made from 13 mL (2 M, 26 mmol) of *n*-butyllithium, 4.1 g (36 mmol) of KO*t*-Bu, and 0.67 g (5.0 mmol) of I, was cooled to −78 °C, and CH_3I (7.0 mL, 112 mmol) was added dropwise. The reaction mixture was treated as described above: yield 0.68 g; IR ($CHCl_3$) 3100–2900 (br, =CH stretch, saturated CH stretch), 1684 (CO stretch), 1600 (C=C stretch, benzene ring), 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7–8 (m), 3.9 (s), 2.5–2.6 (d), 2.1 (s), 1.2–1.5 (m) (NMR is too complex to assign absorptions).

Iodine Doping. All conductivity measurements, using the two-probe method, were performed under argon. The polymers were pressed at 20 000 psi into pellets to measure their conductivity in the pristine state. To measure the conductivity of the doped polymers, the powdered polymers were placed in the doping chamber containing iodine. The chamber was evacuated for 30 min to remove air; after 4 h, the doped powdered polymers were removed and pressed into pellets, and their conductivities were measured. To measure the saturated limits of the conductivities, the above pressed pellets were further exposed to iodine vapors and kept in the iodine chamber until no further increase in conductivity was observed. In the case of V, the doped pellet was evacuated for 24 h before measuring its conductivity. The conductivity data are given in Table I.

Interpretation of Results

Synthesis and Doping of PPV Derivatives. Benzoin yields the dianion with KO*t*-Bu in THF or DMSO,[19] but when the dianion generated by using either KO*t*-Bu–THF or *n*-butyllithium–THF was treated with acetyl chloride, only the starting material, benzoin, was recovered. When Schlosser's base[15] was used to generate the benzoin dianion, the reaction with acetyl chloride yielded stilbene diol diacetate, evidenced by the IR carbonyl band at 1760 cm^{-1} and the loss of OH absorption at 3500 cm^{-1}. The NMR singlet at δ 2.2 ppm (6 protons) and multiplet at δ 7–8 ppm (10 protons) confirm the structure. Obtaining the dimethoxy derivative required the use of dimethyl sulfate. The reaction of benzoin dianion with methyl iodide yields instead the C-methylated methoxy ketone (Scheme II), as evidenced by the presence of a carbonyl band at 1684 cm^{-1} and two methyl NMR singlets at δ 3.5 ppm (3 protons) and 1.5 ppm (3 protons). The reason for this reaction may be explained on the basis of hard and soft acid–base theory.[20]

Reaction of one of the oxygens of the dianion with CH_3I results in the formation of the enolate VII, which can yield O- or C-alkylation. I^- is a soft base whereas AcO^- and OSO_2OCH_3 are hard bases. Hence, the enolate favors O-alkylation when the nucleophile is $CH_3OSO_2O^-$ and C-alkylation when the nucleophile is I^-. Similar observations were made by Inoue et al.[21] in the stereoselective synthesis of α,β-dimethoxystilbene.

I could not be oxidized to II according to the published procedure.[14] Even $CuSO_4$–pyridine–air oxidation proved ineffective. I could only be oxidized by using a large excess of HNO_3–H_2O and refluxing for 3 days, at which time the OH band in the infrared spectrum had disappeared.

The solvent for this reaction proved to be a problem: DMSO reacts with Schlosser's base, and the isolation of either starting material or desired product proved ineffective except for the isolation of a strong smelling yellow compound, probably a sulfur compound, whose characterization was not pursued. With THF alone, starting material was recovered; with ethylene carbonate, the reaction seemed to proceed to some extent, as indicated by IR analysis, but the isolation of a pure product in good yield was possible only when HMPT was used as solvent.

The structure of IV was indicated by its IR and ^1H NMR spectra. Two new bands were formed at 1750 cm^{-1} (C=O, CH_3CO^-) and 1250 cm^{-1} (COC, ester). In the NMR spectrum only two resonances were observed, 7–8 ppm

Table I
Conductivity of Iodine-Doped PPV Derivatives

polymer	conductivity, (S/cm) pristine	after 4 h	after 24 h	dopant addition, mol %
PPV diacetate	10^{-10}	10^{-10}	10^{-10}	*a*
PPV dimethyl ether	10^{-10}	10^{-7}	10^{-6}	36

[a] We did not measure dopant addition in this case since no increase in conductivity was observed.

(br, 4.7 protons) and 2.2 ppm (br, 6 protons). Also in the case of V, two absorptions in the NMR spectrum were visible at 7–8 ppm (br, 4.6 protons) and 3.9 ppm (br, 6 protons). The IR spectrum of V did not show any broad absorption near 1684 cm^{-1}, indicating that the C=O group had disappeared, but there was a broad band at 1250 cm^{-1} (COC, ether).

The low percentage of carbon in the elemental analysis of the polymers seems due to the slow combustion of the materials while performing the C,H analysis. When polymer samples were burned at the hottest part of a Bunsen burner flame, it took, after the quick initial burning, almost 3 min for the residue to disappear completely. This is a frequently observed phenomenon and has been reported for polyaniline.[22] Also, reactions on polymers rarely go to 100% conversion, which can account for the improper ratio of aromatic protons to methyl protons in the NMR spectra of both IV and V.

For the methylation reaction on I, dimethyl sulfate had to be used because CH_3I gave a mixture of products as shown by the IR carbonyl band at 1684 cm^{-1}, a COC band at 1250 cm^{-1}, and a complex NMR spectrum.

PPV does not show an increase in conductivity on exposure to iodine.[6] However, V shows a significant increase in conductivity on exposure to I_2.[10] This has been explained by the lower oxidation potential that results from the presence of the electron-donating methoxyl group. In our study, V shows an increase in conductivity on doping with I_2, whereas IV does not (Scheme III).

The positive charge in V is stabilized by resonance. In the diacetate derivative, the carbonyl carbon induces a positive charge on the adjacent atoms, destabilizing the radical cation and raising the oxidation potential.

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